H10.8

The Influence of Annealing Temperature and Doping on the Red/Near-Infrared Luminescence of Ion Implanted SiO_2:nc-Si

D.I. TETELBAUM, V.A. BURDOV, S.A. TRUSHIN, and A.N. MIKHAYLOV
Physico-Technical Research Institute of Nizhnii Novgorod State University, 603950,
Nizhnii Novgorod, Gagarin prospect, 23/3, Russia

D.G. REVIN, and D.M. GAPONOVA
Russian Academy of Science Institute of Physics for Microstructures, 603600 Nizhnii
Novgorod, GSP – 105, Russia

ABSTRACT

The results of an experimental research of the dependence of photoluminescence (PL) intensity in region about 800 nm for silicon nanoinclusions (quantum dots) obtained by Si ion implantation in SiO_2 on the dose of Si ions at two temperatures of an annealing T_{ann} = 1000 and $1100°$ C are presented. It is established that in both cases the dependences have the shape of the curves with a maximum. For $1100°$ C the maximum is shifted to the lower dose. The influence of an additional ion doping by the phosphorus on intensity of PL is investigated depending on the dose (concentration) of P and the dose of the silicon at T_{ann} = $1000°$ C. It is shown, that in all the investigated region of P doses, the presence of P enhances the PL. The degree of the enhancement increases with the P dose, but the rate of the intensity enhancement goes down. With the growth of Si dose at the constant dose of P, the degree of the enhancement decreases. In an approximation of an effective mass, the energy spectra of a quantum dot are calculated at the presence of one or several P atoms for various their arrangement.

INTRODUCTION

The system of silicon nanoinclusions (NI) in SiO_2 (SiO_2:nc-Si) attracts the great attention in connection with the prospects of its use in the silicon optoelectronics. Ion implantation is one of the most common methods of the SiO_2:nc-Si production [1-5]. The important parameter is the intensity of the photoluminescence (IPL) for the constant intensity of the excitation. This is especially important taking into account a small thickness of nc-Si layer for ordinarily ion energies. Generally, IPL depends on the several factors: NIs number, their sizes, the availability and the concentration of the centers of a nonradiative recombination. These factors are sensitive to the conditions of the ion implantation (ion energy and dose), the conditions of the annealing (temperature and time), and also the presence of the impurities. In [6,7] was shown that for a fixed annealing temperature T_{ann} = $1000°$ C (the annealing time, t_{ann} = 2 hours), IPL can be adjusted by the choice of a dose. At that, the sizes of NI practically do not vary, and their density grows. The IPL growth proceeds up to the dose for which the NI joining begins due to their high concentration. Also, it was established that IPL can be essentially increased by the additional implantation of phosphorus. The position of the PL peak occurs practically independent on the phosphorus doses. In the report, the results of a prolongation of these investigations are presented. The dependence of IPL on the dose of silicon was taken at the more high temperature of an annealing – $1100°$ C. The influence of the doping by P was investigated depending on Si and P dose. The theoretical research of the influence of impurity atoms contained in the quantum dots (QD) on the energy spectra and on the energies of the radiative interband transitions is continued.

EXPERIMENTAL

The SiO_2 layers with the thickness of 300 - 600 nm were grown up on the silicon in a "dry – wet – dry" cycle. Ion implantation by Si^+ and P^+ was provided at the energy of ions $E = 150$ keV and the ion current densities $j < 3$ $\mu A/cm^2$. The postannealing was carried out in the dry nitrogen atmosphere. The photoluminescence (PL) spectra were measured at the Ar laser excitation ($\lambda = 488$ nm) with a power density about 50 W/cm^2.

RESULTS AND DISCUSSION

For all the annealed after the Si^+ implantation layers, the PL spectra with a maximum close to 800 nm are observed. Such spectrum is typical for Si NIs in SiO_2 [1-6]. In Fig.1, the IPL dependencies on the Si dose at the $T_{ann} = 1000$ and 1100° C are presented. Earlier, it was shown [7] that for $T_{ann} = 1000^\circ$ C, the dependence well coincides with the calculated one. This calculation was made on the base of the model of the NI accumulation with the dose
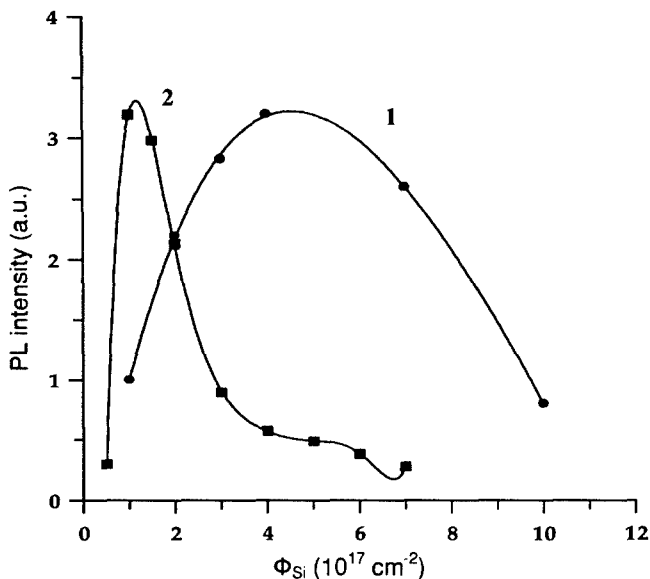

Fig.1. The silicon dose (Φ_{Si}) dependencies of PL peak intensity at two annealing temperatures. T_{ann}: 1 – 1000° C, 2 – 1100° C.

and NI joining at higher doses. It is evident that for 1100° C the IPL dependence on the dose has a similar shape – the curve with the maximum, but the position of the maximum is shifted to the lower doses. It is naturally to explain by the fact that the rate of NI nucleation increases with the annealing temperature, therefore for the same concentration of the excess silicon atoms, the NI density is higher. However, the model used earlier for $T_{ann} = 1000^\circ$ C does not allow to explain quantitatively the IPL dependence on the dose for $T_{ann} = 1100^\circ$ C. Perhaps, it is necessary to take into account other factors, such as Ostwald rippening, the role of which would increase with T_{ann}.

In Fig.2, the dependence of $F = I_p/I_{wp}$ (the ratio of IPL for SiO_2:nc-Si additionally doped by phosphorus and those versus without phosphorus doping) on phosphorus dose is shown.
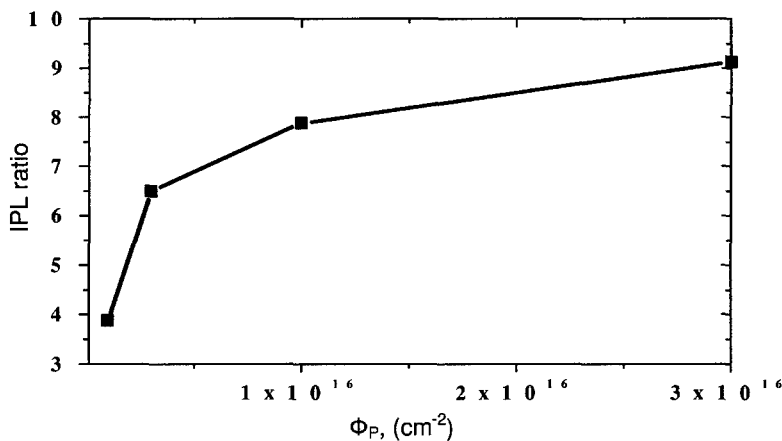
Fig.2. The phosphorus dose (Φ_P) dependence of $F = I_p/I_{wp}$ (the ratio of IPL for SiO_2:nc-Si additionally doped by phosphorus and those versus without phosphorus doping. $\Phi_{Si} = 1\cdot10^{17}$ cm^{-2}, $T_{ann} = 1000^\circ$ C.

With growth of the dose, the F magnitude increases. In [6,7], the model is suggested according to which the IPL enhancement at the phosphorus doping is connected with the action of two mechanisms: the passivation of the disrupted bonds (hence, the decrease of the nonradiative recombination rate) and the appearance of additional electrons in the conductivity band of QD. In our case, unlike [5], the decrease of the IPL at the high P concentration is not observed.

In Fig.3, the F dependence on the Si dose at the constant P dose is presented. The decrease of F with Si dose can be caused by the reduction of P atoms number contained in each NI with the increase of the amount of the latter. This is possible if a redistribution of the phosphorus between SiO_2 and NIs during the annealing takes place.
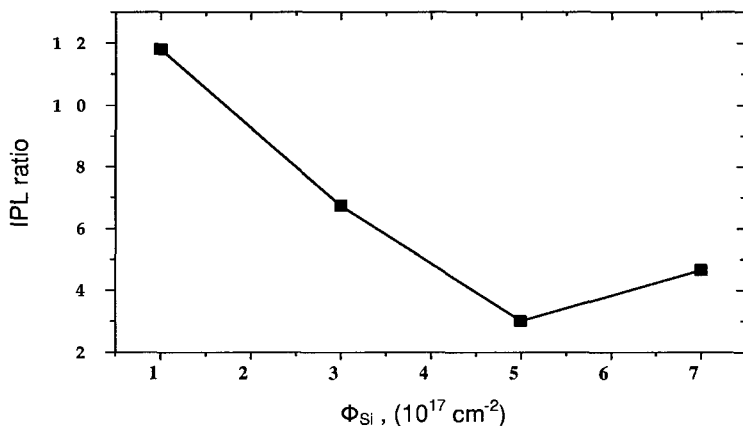

Fig.3. The dependence of $F = I_p/I_{wp}$ (IPL ratio) on the Si dose (Φ_{Si}). $\Phi_P = 1\cdot10^{16}$ cm^{-2}, $T_{ann} = 1000^\circ$ C.

THEORETICAL ACCOUNTS

To prove theoretically the absence of the essential shifts of the PL peak at the doping by phosphorus, the calculations of the electronic energy spectra and of the optical gap of QD in the envelope function approximation were carried out. For solving the problem we were made the following assumptions: 1) the quantum dots have the spherical shape; 2) the impurity ions create a field of a hydrogen-like type; 3) spin-orbit interaction can be neglected; 4) the silicon quantum dots are placed in a dielectric matrix.

For the definition of energy levels we must solve the equation for the envelope functions $F_\mu(\vec{r})$

$$\hat{H}_{\mu\nu} F_\nu(\vec{r}) = E F_\mu(\vec{r}), \tag{1}$$

where E is the electron energy which is counted off the top of the valence band, and operator $\hat{H}_{\mu\nu}$ represents the single-electron Hamiltonian which was written in a $\vec{k} \cdot \vec{p}$-approximation. Near the X-point in a conduction band the Hamiltonian is represented by a 2×2 matrix:

$$\begin{pmatrix} \hat{H}_{0c} + \dfrac{\hbar^2}{6}\left(\dfrac{1}{m_t}-\dfrac{1}{m_l}\right)\left(\hat{k}^2-3\hat{k}_z^2\right)+\hat{V}_c & \hbar^2\left(\dfrac{1}{m_t}-\dfrac{1}{m_0}\right)\hat{k}_x\hat{k}_y+i\dfrac{\hbar^2 k_0}{m_l}\hat{k}_z \\[3mm] \hbar^2\left(\dfrac{1}{m_t}-\dfrac{1}{m_0}\right)\hat{k}_x\hat{k}_y-i\dfrac{\hbar^2 k_0}{m_l}\hat{k}_z & \hat{H}_{0c}+\dfrac{\hbar^2}{6}\left(\dfrac{1}{m_t}-\dfrac{1}{m_l}\right)\left(\hat{k}^2-3\hat{k}_z^2\right)+\hat{V}_c \end{pmatrix}$$

Here

$$\hat{H}_{0c} = \Delta_{\Gamma X} + \dfrac{\hbar^2 \hat{k}^2}{2m_c}$$

is the isotropic operator with the electronic effective mass $m_c = 3m_t m_l/(2m_l + m_t)$, where m_t and m_l are the "transverse" and "longitudinal" mass respectively. These masses equal $0.19 m_0$ and $0.92 m_0$. Value $k_0 = 0.144 \cdot 2\pi/a$ is determining the distance in $\vec{k}$-space between X-point and the nearest minimum of the energy in Brillouin zone, $a = 0.54$ nm - the lattice constant, $\Delta_{\Gamma X} = 1.21$ eV is the difference between the energies in X-point of the conduction band and in Γ-point of the valence band. $\hat{V}_c$ is the operator of Coulomb interaction which can be written as

$$\hat{V}_c = -\sum_{j=1}^{K}\dfrac{e^2}{\varepsilon_s|\vec{r}-\vec{h}_j|} - \dfrac{e^2(\varepsilon_s-\varepsilon_d)}{\varepsilon_s R}\sum_{j=1}^{K}\sum_{l=0}^{\infty}\dfrac{h_j^l r^l}{R^{2l}}\dfrac{l+1}{l\varepsilon_s+(l+1)\varepsilon_d}P_l(\cos\theta_j) +$$

$$\dfrac{e^2(\varepsilon_s-\varepsilon_d)}{2\varepsilon_s R}\sum_{l=0}^{\infty}\dfrac{r^{2l}}{R^{2l}}\dfrac{l+1}{l\varepsilon_s+(l+1)\varepsilon_d}.$$

It consists of two part: the direct Coulomb interaction between electron and impurity ions, and the interaction between electron and two image fields - of ions and of electron itself. $\vec{h}_j$ is the radius-vector of the impurity ion with the number j, parameters ε_s and ε_d are the dielectric constants of silicon and dielectric matrix, R is the dot radius, $-e$ is the electron charge, K is he number of the impurity ions and $P_l(\cos\vartheta_j)$ is a Legendre polynomial.

Near the Γ-point in a valence band the Hamiltonian is represented by a 3×3 matrix

$$
\begin{pmatrix}
\hat{H}_{0h} + \hat{V}_x + \hat{V}_c & -N\hat{k}_x\hat{k}_y & -N\hat{k}_x\hat{k}_z \\
-N\hat{k}_x\hat{k}_y & \hat{H}_{0h} + \hat{V}_y + \hat{V}_c & -N\hat{k}_y\hat{k}_z \\
-N\hat{k}_x\hat{k}_z & -N\hat{k}_y\hat{k}_z & \hat{H}_{0h} + \hat{V}_z + \hat{V}_c
\end{pmatrix}
$$

Here

$$
\hat{H}_{0h} = -\frac{\hbar^2\hat{\vec{k}}^2}{2m_h}, \quad \hat{V}_j = \frac{\hbar^2}{2m_0}\frac{L-M}{3}\left(\hat{\vec{k}}^2 - 3\hat{k}_j^2\right)
$$

and m_h is the hole effective mass which equals $3m_0/(L+2M)$. The numbers L, M, N are the empirical parameters which equal 6.8, 4.43, 8.61 respectively [8].

The Hamiltonian $\hat{H}_{\mu\nu}$ takes into account the real silicon band structure possessing rather strong anisotropy. However, in spite of this, the anisotropy of the dispersion law can be described by means of a perturbation theory, as well as a Coulomb interaction with impurity ions.

Solving equation (1) we find the several lowest energy levels in the conduction band and several highest energy levels in the valence band and also their dependence on number K for different types of an impurity distribution. Then the change of the optical gap Δ due to the presence of an impurity in the quantum dot can be written as

$$
\delta(K,\vec{h}) = \Delta(K,\vec{h}) - \Delta(0), \tag{2}
$$

where vector $\vec{h}$ means the set $(\vec{h}_1; \vec{h}_2; \dots \vec{h}_K)$.

The results of our calculations are presented in the Table. The gap $\Delta_\infty(0)$ corresponds to the case when the potential barriers height is assumed infinite. In this case the magnitude of the optical gap without impurity has the greatest value. If we have taken into account the finite height of the barriers (3.1eV for electrons and 4.4eV for holes), the gap will be less ($\Delta_1(0)$ in the Table.1). The smallest values of the gap are obtained when we take into account not only the finite height of the barriers, but also the discontinuity of the effective mass on the boundary of the quantum dot. The gap $\Delta_2(0)$ was calculated for the case when the electron effective mass in the dielectric matrix equals m_0 and does not coinsides with the masses m_e or m_h in the silicon quantum dot. As we can see, the differences between $\Delta_\infty(0)$ and $\Delta_2(0)$ are rather significant. Note that the values

$\Delta_2(0)$ for different sizes of the quantum dot are in good agreement with the experimental data [9,10,11] and with the theoretical calculations of other authors who used another methods (such as local density approximation [12], tight-binding model [13,14] or pseudopotential method [15,16]).

The calculations of the optical gap shift $\delta(K, \vec{h})$ were carried out in the framework of more simple model with the infinite barriers. Another models with the finite height of the barriers are significantly more complicated for the calculations, and as the estimations have shown, the results do not differ essentially. The position of the energy levels and hence the value δ will be depend not only on the quantity of donors but also on the distribution of ions inside the quantum dot. Since it is impossible to obtain the analitical expression for the shift δ in a general case, we consider a three kinds of impurity distribution which correspond to some extreme situations.

Table.1. The magnitudes of the optical gaps (Δ) and its shifts (δ) due to the presence of the impurity atoms (eV) for different values of radius (nm).

R	$\Lambda_r(0)$	$\Lambda_l(0)$	$\Lambda_2(0)$	δ_1			δ_2		
				$K=1$	$K=3$	$K=5$	$K=1$	$K=3$	$K=5$
1.5	2.63	2.28	1.90	-0.04	-0.12	-0.21	-0.08	-0.30	-0.55
2	1.98	1.83	1.64	-0.03	-0.09	-0.15	-0.06	-0.23	-0.42
2.5	1.69	1.61	1.50	-0.02	-0.07	-0.12	-0.05	-0.18	-0.34

One of these is the case, when impurity ions distributed by the centrally-simmetric way on the boundary of the quantum dot ($h_j = R$). As the calculations have shown, in this case $\delta = 0$ irrespective of the donors number K. In the other case, when all the impurity atoms are situated at the centre of the quantum dot ($h_j = 0$, actually $h_j \ll R$), the shift δ, which is denoted by δ_1 in the Table, is nonzero. The last case corresponds to the maximum asymmetric distribution with the maximum electrical dipole momentum, when all the impurity atoms are situated in one place on the boundary of the quantum dot. This distribution type gives more significant shift δ_2 (see the Table.1).

As it has been seen from the table the magnitude of the shift is rather small almost in all cases, shown in the Table, excluding the case of the maximum asymmetric distribution with the large number of donors ($K = 5$). However, it is clear, that this kind of the distribution is hardly realized in experiments and the possibility of such configurations strongly decreases with increasing K. Hence, the contribution of the asimmetric configurations with the maximum dipole momentum will be negligible.

In reality, the impurity atoms, perhaps, are randomly situated inside the NI. Therefore, the true magnitude of δ for $K \le 5$ woukd be somehow averedged one between ~ -0.2eV and zero, e.g. $-0.1eV < \delta < 0$. For the case $K \gg 1$, the consideration becomes not justified enough because: (i) the interaction between impurity atoms must be taken into account (the approximation of isolated atoms can be not right); (ii) the validity of the perturbation theory can be violated.

Thus, the magnitude δ, obtained experimentally, can not exceed a several per cents from the magnitude of the gap and the shift of the luminescence peak in the presence of phosphorus must be rather small.

CONCLUSIONS

1. The dependences of IPL from Si doses similar character for $T_{ann}=1000^0C$ and 1100^0C. However, for the latter case, unlike the first one, it can not be quantitively described by the same model.
2. The additional phosphorus implantation causes the IPL enhancement for all the impurity doses investigated.
3. The effectivity of phosphorus related IPL enhancement drops with the silicon dose (excess silicon concentration)
4. Theoretical consideration in effective mass approximation shows that (in agreement with experiment) the phosphorus doping would not shift the luminescent peak position significantly for the interband transitions.

AKNOWLEDGEMENTS

REFERENCES

1. P. Mutti, G. Ghislotti, S. Bertoni, L. Bonoldi, G.F. Cerofolini, L. Meda, E. Grilli, M. Guzzi, Appl. Phys. Lett., 66, 851, (1995).
2. T. Shimizu-Iwayama, K. Fujita, S. Nakao, K. Saitoh, R. Fujita, N. Itoh, J.Appl.Phys., 75, 7779, (1994).
3. K. S. Min, K.V. Scheglov, C.M. Yang, H. A. Atwater, M.L. Brongersma, A. Polman, Appl. Phys. Lett., 69, 2033, (1996).
4. G.A. Kachurin, I.E. Tischenko, K.S. Zhuravlev, N.A. Pazdnikov, V.A. Volodin, A.K. Gutakovsky, A.F. Leiser, W. Skorupa, R.A. Yankov, Nucl. Instr. Meth. B, 122, 571, (1997).
5. M. Fujii, A. Mimura, S. Hayashi, K. Yamamoto, Appl. Phys. Lett., 75, 184, (1999).
6. D.I. Tetelbaum, O.N.Gorshkov, S.A.Trushun, D.G.Revin, D.M.Gaponova, W. Eckstein, Nanotechnology, 11, 295, (2000).
7. D.I. Tetelbaum, S.A. Trushin, V.A. Burdov, A.I. Golovanov, D.G. Revin, D.M. Gaponova, B, 174, 123, (2001).
8. M. Voos, Ph. Uzan, C. Delalande, G. Bastard, A. Halimaoui, Appl. Phys. Lett., 61, 1213, (1992).
9. A. Mimura, M. Fujii, S. Hayashi, D. Kovalev, F. Koch, Phys. Rev. B, 62, 12625, (2000).
10. S. Takeoka, M. Fujii, S. Hayashi, Phys. Rev. B, 62, 16820, (2000).
11. S. Guha, B. Quadri, R.G. Musket, M.A. Wall, T. Shimizu-Iwayama, J. Appl. Phys., 88, 3954, (2000).
12. B. Delley, E.F. Steigmeier, Appl. Phys. Lett., 67, 2370, (1995).
13. S. Y.Ren, J.D. Dow, Phys. Rev. B, 45, 6492, (1992).
14. C. Delerue, M. Lannoo, G. Allan, Phys. Rev. Lett., 84, 2457, (2000).
15. S. Ogut, J.R. Chelikowsky, Phys. Rev. Lett., 79, 1770, (1997).
16. A. Franceschetti, A. Zunger, Phys. Rev. B, 62, 2614, (2000).